Laser Original**Nonlinear Spectroscopic Ellipsometry
of Isotropic Media****Igor I. GANCHERYONOK*†**

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We are developing a novel method of nonlinear polarization spectroscopy which we term NSE (Nonlinear Spectroscopic Ellipsometry). NSE deals with investigations of the polarization behavior of a probe beam passing through an isotropic medium in the presence of a strong pumping field. The probe wave polarization parameters are derived in the case of arbitrary polarized interacting waves in the framework of the 3rd-order nonlinear susceptibility (3NS). A new method of measuring the phase of the 3NS that is based on the use of circularly polarized probe and linearly polarized pump beams is proposed. The feasibilities of separate measurements of the dispersion of the real and imaginary parts of the 3NS by the NSE methods are demonstrated. The results of the theoretical consideration are applied to estimate the magnitude of the 3NS of some dye solutions and gaseous media under different conditions of excitation.

Key Words: Linear, Circular and elliptic polarization, Spectroscopy, Nonlinear susceptibility, Ellipsometry

1. Introduction

When fairly high-power polarized radiation propagates in an isotropic medium, an induced anisotropy may arise due to the nonlinear character of the interaction. This anisotropy can significantly affect the polarization of the probe field as well as the character of the change of its intensity. The cited effect lies in the basis of nonlinear polarization spectroscopy (NPS) of initially isotropic media. In the standard scheme of NPS the two beams [pumping beam at frequency ω_0 (wavelength λ_0) and probe wave at frequency ω_1 (λ_1)] with different polarizations are incident upon absorbing sample. Usually the pump wave has a linear or circular polarization and the

probe one is linearly polarized^{1,2}. The strong field creates an intensity and frequency-dependent birefringence and dichroism (light-induced anisotropy (LIA)). As a result, the nonlinear interaction in the medium with LIA produces a polarization component at the probe frequency that is orthogonal to the initial probe polarization. This new polarization component then can be detected by a crossed analyzer. Some small rotation of the analyzer is adapted to detect small signals with high sensitivity³. When the rotation angle changes from zero (a perfectly blocked position) to 90 degrees, the signal of NPS is transformed into the signal of saturation spectroscopy⁴. More general case occurs when the pump beam has an elliptical polarization.

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Such investigations can be counted on the fingers of one hand. Levenson et al⁽⁵⁾ have investigated the line shape of Raman-induced Kerr effect (RIKE) resonances with elliptical pump polarization. Bergmann et al⁽⁶⁾ applied the elliptically polarized pump field for study RIKE in active and anisotropic crystals. Ref.7 demonstrates the performance of the rotation free measurements by using exciting light with proper elliptical polarization. Some theoretical suggestions of spectroscopic applications of elliptically polarized pump can be founded in ref. 8 and 9. And, to the authors knowledge, there are no papers devoted to the polarization behavior of a weak field on passing through isotropic medium in the presence of a strong field with arbitrary elliptical polarization. On the other hand, such investigations in coherent anti-Stokes Raman spectroscopy (CARS) revealed some advantages in comparison with conventional CARS⁽¹⁰⁾. This technique (coherent Raman ellipsometry technique of Akhmanov) is based on the measurement of the dispersion of the polarization parameters of the CARS signal as the frequency detuning of interacting waves is scanned.

In the present work we will derive the polarization changes of arbitrary polarized probe wave interacting with nonlinear medium excited by an arbitrary polarized pumping wave (Nonlinear Spectroscopic Ellipsometry). Then, using our theoretical results we will represent the numerical estimations of magnitude of the nondegenerate 3rd-order nonlinear susceptibility (3NS) of some substances.

2. Analysis

2.1 General Formalism

Let two waves propagate in a resonance medium in the Z direction. Assuming both waves to be quasi-monochromatic and quasi-plane, we can describe the change in their complex ampli-

tudes $\vec{E}_j$ by the equations^{11,12)}

$$\hat{L}\vec{E}_j + \frac{\sigma_j}{2}\vec{E}_j = \frac{i\omega_j\mu_0 c}{2n_j}\vec{P}_j^{NL}, \quad (1)$$

where $\hat{L} = \frac{\partial}{\partial z} + \frac{n_j}{c}\frac{\partial}{\partial t}$ is a differential operator; σ_j and n_j are the linear absorption coefficient and refractive index of the medium at the frequency ω_j ($j = 0$ -pump wave, $j = 1$ -probe wave), respectively; $\vec{P}_j^{NL}$ is the amplitude of the nonlinear polarization of matter. Equations (1) are valid under the condition of the so-called slowly-varying amplitude and phase approximation, which plays a central role in quantum optics¹³⁾. Further we restrict our consideration by the steady-state limit ($\frac{\partial \vec{E}_j}{\partial t} = 0$) and the 3rd-order perturbation theory. Then from eqs. (1) for the probe beam evolution we have the following equation

$$\frac{d\vec{E}_1}{dz} + \frac{\sigma_1}{2}\vec{E}_1 = \frac{i\omega_1\mu_0 c}{2n_1}\vec{P}_1^{(3)}, \quad (2)$$

where $\vec{P}_1^{(3)}$ is

$$\vec{P}_1^{(3)} =$$

$$\epsilon_0 K \chi^{(3)}(\omega_1; \omega_1, \omega_0, -\omega_0) / \vec{E}_1 \vec{E}_0 \vec{E}_0^* \quad (3)$$

Here K is the numerical factor which in our case is equal to $3/2^{12)}$.

Let us to introduce a LIA tensor $\hat{S}^{14)}$

$$\hat{S} = \hat{I} + C_1 \vec{e}_0 \otimes \vec{e}_0^* + C_2 \vec{e}_0^* \otimes \vec{e}_0, \quad (4)$$

where $\hat{I}$ is the unit tensor; $\vec{e}$ is polarization vector of the intense field; asterisk and $\otimes$ denote the complex conjugation and direct product respectively; the complex, in general case, parameters C_1 and C_2 are defined in terms of the 3NS tensor

$$C_1 = \chi_{1122} / \chi_{1221}, \quad C_2 = \chi_{1212} / \chi_{1221}. \quad (5)$$

Further in this article we will analyze only the media with a hermitian tensor $\hat{S}$, i. e. C_1 and $C_2 \in \text{Re}$. The results for a nonhermitian $\hat{S}$ will be

published elsewhere. Then the relationship between the polarization and fields (3) becomes

$$\vec{P}_1^{(3)} = \frac{3}{2} \epsilon_0 \chi_{1221} / |\vec{E}_0|^2 \hat{S} \vec{E}_1. \quad (6)$$

When eq. (6) is substituted in eq. (2), we have

$$\begin{aligned} \frac{d\vec{E}_1}{dz} + \frac{\sigma_1}{2} \vec{E}_1 &= i \frac{3}{4} \frac{\omega_1}{cn_1} \chi_{1221} / |\vec{E}_0|^2 \hat{S} \vec{E}_1 \\ &= a \hat{S} \vec{E}_1 \end{aligned} \quad (7)$$

or

$$\frac{d\vec{E}_1}{dz} = (a \hat{S} - \frac{\sigma_1}{2} \hat{I}) \vec{E}_1 = \hat{N} \vec{E}_1. \quad (8)$$

Here, following to the general theory of propagation of polarized light in anisotropic media¹⁵⁾, we introduced a 2x2 matrix $\hat{N}$. This matrix is the differential propagation Jones matrix that characterizes the anisotropic properties of the medium over the transverse plane at Z . Azzam et al.¹⁶⁾ have shown that in the case when the evolution of the vector amplitude is described by the differential equation in the form (8) the behavior of polarization state of the light beam can be examined separately. The corresponding equation is given as

$$\frac{d\chi_1}{dz} = -N_{12} \chi_1^2 + (N_{22} - N_{11}) \chi_1 + N_{21}, \quad (9)$$

where N_{ij} are the elements of the Jones matrix $\hat{N}$; χ_1 is the complex variable which determines the polarization state of the probe beam and has the following form

$$\chi_1 = E_{1v}/E_{1u}. \quad (10)$$

Here E_{1u} and E_{1v} are the components of vector $\vec{E}_1$ along a pair of basis states of polarization $\vec{u}$ and $\vec{v}$. In our case for the elements N_{ij} we get

$$N_{ij} = a S_{ij} - \frac{1}{2} \sigma_1 \delta_{ij}. \quad (11)$$

Substituting the terms of eqs. (11) into eq. (9)

gives

$$\frac{d\chi_1}{dz} = -a S_{12} \chi_1^2 + a (S_{22} - S_{11}) \chi_1 + a S_{21}. \quad (12)$$

Eq. (12) shows that the evolution of the polarization state of the probe beam does not depend on the linear absorption in the resonance medium. In our case the matrix $\hat{N}$ is the function of the distance z due to the strong field depletion, and eq. (12) is the general Riccati equation. However it can be considerably simplified in the basis of the eigenvectors of the tensor $\hat{S}$. Then $\hat{S}$ becomes the diagonal matrix $\hat{S}'$

$$\hat{S}' = \begin{pmatrix} S_1 & 0 \\ 0 & S_2 \end{pmatrix}$$

and eq. (12) reduces to the form

$$\frac{d\chi_1}{dz} = a (S_2 - S_1) \chi_1 = a \Delta S \chi_1. \quad (13)$$

This is homogeneous linear differential equation of the first order and its solution is

$$\chi_1(z) = \chi_{10} \exp [\Delta S A(z)], \quad (14)$$

where

$$A(z) = i \frac{3}{4} \frac{\omega_1}{cn_1} \chi_{1221} \int_0^z |\vec{E}_0(\xi)|^2 d\xi \quad (15)$$

and χ_{10} defines the initial state of polarization at $z=0$.

Now the evolution of the two parameters of the ellipse of polarization of the probe field, the azimuth Θ_1 and the ellipticity H_1 can be easily obtained from the function $\chi_{10}(z)$. When basis states of polarization $\vec{u}$ and $\vec{v}$ are two orthogonal linear polarizations $\vec{e}_x$ and $\vec{e}_y$, Θ_1 and H_1 are obtained from χ_{10} by the following relations¹⁵⁾

$$\tan 2\Theta_1 = \frac{2\operatorname{Re}\chi_1}{1 - |\chi_1|^2}, \quad (16)$$

$$\sin 2\epsilon_1 = \frac{2\operatorname{Im}\chi_1}{1 + |\chi_1|^2}, \quad (17)$$

where ϵ_1 is the angle of ellipticity and is related to the ellipticity η_1 by

$$\eta_1 = \tan \epsilon_1. \quad (18)$$

In the basis of circular polarizations ($\vec{e}_+$, $\vec{e}_-$) the expressions for Θ_1 and η_1 become

$$\Theta_1 = \frac{1}{2} \arg(\chi_1), \quad (19)$$

$$\eta_1 = \frac{|\chi_1| - 1}{|\chi_1| + 1}. \quad (20)$$

In general case of arbitrary basis vectors we will use a bilinear transformation $\chi_{1uv} \rightarrow \chi_{1xy}$ which is given by

$$\chi_{1xy} = (f_{22}\chi_{1uv} + f_{21}) / (f_{12}\chi_{1uv} + f_{11}). \quad (21)$$

Here f_{ij} are the elements of the matrix $\hat{F}$ formed by the eigenvectors $\vec{u}$ and $\vec{v}$ as the column vectors, in other words

$$\hat{F}^{-1} \hat{S} \hat{F} = \hat{S}'. \quad (22)$$

As we continue our consideration we go on to describe at the beginning the cases of the linearly and circularly polarized pump beam and then to analyze the general case of arbitrary elliptical polarization.

2.2 Linearly Polarized Pump

In this case eq. (4) is transformed to the form

$$\hat{S} = \hat{I} + (C_1 + C_2) \vec{e}_0 \otimes \vec{e}_0. \quad (23)$$

This means that $\hat{S}$ is diagonal matrix in the Cartesian basis $\vec{e}_x$ and $\vec{e}_y$. The eigenvalues are equal to

$$S_1 = 1 + C_1 + C_2, S_2 = 1$$

$$\text{and } \Delta S = -(C_1 + C_2). \quad (24)$$

In the general case of initial elliptical polarization of the probe beam we have

$$\chi_{10} = \frac{\tan \Theta_{10} + i \tan \epsilon_{10}}{1 - i \tan \Theta_{10} \tan \epsilon_{10}}, \quad (25)$$

where Θ_{10} and ϵ_{10} are the corresponding values of azimuth from the X axis and ellipticity angle. Let us introduce the following notations

$$\begin{aligned} A(z) &= \beta(-\operatorname{Im}\chi_{1221} + i \operatorname{Re}\chi_{1221}) \\ &= \Lambda' + i\Lambda'' = \Lambda. \end{aligned} \quad (26)$$

Now, substituting eqs. (24) - (26) into eq. (14) and then using eqs. (16) - (17), we can calculate the polarization parameters of the probe beam. However the results are cumbersome and difficult to inspect. We therefore consider only the cases of a linearly, circularly and elliptically ($\Theta_{10} = 0$ or $\pi/2$) polarized probe beam.

2.2.1 Linearly polarized probe beam

In this case $\chi_{10} = \tan \theta_{10}$. Then, using eqs. (14) and (26) we can get from eqs. (16) - (17) the following expressions

$$\tan 2\Theta_1 = \frac{2 \tan \Theta_{10} \exp(\Delta S \Lambda') \cos(\Delta S \Lambda'')}{1 - \tan^2 \Theta_{10} \exp(2\Delta S \Lambda')}, \quad (27)$$

$$\sin 2\epsilon_1 = \frac{2 \tan \Theta_{10} \exp(\Delta S \Lambda') \sin(\Delta S \Lambda'')}{1 + \tan^2 \Theta_{10} \exp(2\Delta S \Lambda')}. \quad (28)$$

Eqs. (27) and (28) show that there is an optimum value of input azimuth Θ_{10} when ellipticity η_1 achieves the maximum magnitude

$$|\tan \Theta_{10}^{\text{opt}}| = \exp(-\Delta S \Lambda'). \quad (29)$$

And only in the case of fairly weak interaction ($|\Lambda'| \ll 1$) we can obtain the conventional result¹⁷⁾

$$|\tan \Theta_{10}^{\text{opt}}| \simeq 1 \text{ and } |\Theta_{10}^{\text{opt}}| \simeq \pi/4. \quad (30)$$

It is interesting to note that from eqs. (27) and (28) the oscillatory behavior of the polarization parameters with distance z or intensity of the pump beam is potentially possible. However it hardly can be observed under conditions when only the third order optical nonlinearity is taken into consideration. The realistic pump field attenuation can be a considerable restriction in this case too. In most cases of experimental research the probe wave is linearly polarized at $\Theta_{10}=45^\circ$ to the linear polarization (along $\vec{e}_x$) of the pumping beam. Then eqs. (27) and (28) in approximation that is linear in Δ' and Δ'' ($|\Delta| \ll 1$) can be rewritten as

$$\tan 2\Theta_1 \simeq -(\Delta S \Delta')^{-1}, \quad (31)$$

$$\sin 2\epsilon_1 \simeq \Delta S \Delta'', \quad (32)$$

Taking into account that values Δ' and Δ'' are rather small in accordance with above mentioned approximation from eqs. (31) and (32) we have

$$\Delta\Theta_1 = \frac{\pi}{4} - \Theta_1 \simeq -\frac{\Delta S \Delta'}{2} \sim \text{Im} \chi_{1221} \quad (33)$$

$$\eta_1 \simeq \frac{\Delta S \Delta''}{2} \sim \text{Re} \chi_{1221}, \quad (34)$$

where $\Delta\Theta_1$ is the angle of the rotation of the plane of polarization. Thus, NSE with the linearly polarized probe and pumping beams permit separate measurements of the dispersion of the real and imaginary parts χ_{1221} .

2.2.2 Circularly polarized probe beam

With input circular polarization of the probe field ($\chi_{10} = \pm i$) eqs. (16) and (17) can be reduced to the form

$$\tan 2\Theta_1 = \mp \frac{2\exp(\Delta S \Delta') \sin(\Delta S \Delta'')}{1 - \exp(2\Delta S \Delta')}, \quad (35)$$

$$\sin 2\epsilon_1 = \pm \frac{2\exp(\Delta S \Delta') \cos(\Delta S \Delta'')}{1 + \exp(2\Delta S \Delta')}, \quad (36)$$

where the upper and lower signs correspond to the initial right (R) - and left (L) -handed circular polarization states of the probe waves, respectively. In both cases (i. e., R and L) the initial circular polarization is modified to the elliptical. However the major axes of the ellipse are rotated in opposite directions. It should be noted that in the first order approximation in Δ circular polarization of the probe beam is preserved. In the second order approximation eqs. (35) and (36) are transformed to the form

$$\tan 2\Theta_1 = \pm \frac{\Delta''}{\Delta'} = \mp \frac{\text{Re} \chi_{1221}}{\text{Im} \chi_{1221}}, \quad (37)$$

$$\sin 2\epsilon_1 = \pm [1 - (\Delta S \Delta')^2 - \frac{1}{2} \Delta S^2 |\Delta|^2]. \quad (38)$$

Thus in this case, measuring the azimuth of polarization ellipse of the output probe beam, we can determine the ratio of real and imaginary parts of the nondegenerate 3NS. Recently Ma et al.¹⁸⁾, reported a new method for measuring the phase of the nondegenerate 3NS that is determined by this ratio. Taking into account that the present ellipsometric techniques have reached a very high level of sensitivity¹⁹⁾ we expect that our method can be more precise. Finally we would like to note that in ref.20, as far as we can judge from the published data, the polarization state of the probe beam with input circular polarization is changed in the field of the linearly polarized pump in Hg. However the authors did not take this process into account investigating the polarization properties of the coherent radiation at combined frequency, although parametric coupling between waves practically always occurs¹¹⁾. In ref.21 Keller et al. have demonstrated the new possibilities of pump-probe experiments with the circularly polarized probe beam to observe the Doppler-free birefringence induced in neon gas by a linearly polarized

pumping beam.

2.2.3 Elliptically polarized probe beam ($\Theta_{10}=0$ and $\Theta_{10}=90^\circ$)

In these cases $\chi_{10}=\pm i \tan \epsilon_{10}$ and $\chi_{10}=\pm i \cot \epsilon_{10}$. Here the upper signs correspond to the same handedness of the polarization ellipse as in the pump beam and the lower ones the opposite. Now eqs. (16) and (17) have the forms

$$\tan 2\Theta_1 = \mp \frac{2\Psi \exp(\Delta S \Delta') \sin(\Delta S \Delta'')}{1 - \Psi^2 \exp(2\Delta S \Delta')}, \quad (39)$$

$$\sin 2\epsilon_1 = \pm \frac{2\Psi \exp(\Delta S \Delta') \cos(\Delta S \Delta'')}{1 + \Psi^2 \exp(2\Delta S \Delta')}, \quad (40)$$

where $\Psi = \tan \epsilon_{10}$ or $\cot \epsilon_{10}$.

In approximation that is linear in Δ , the parameters Θ_1 and ϵ_1 can be described by the equations

$$\tan 2\Theta_1 = \mp (\pm) \Delta S \Delta'' \tan \epsilon_{10}, \quad (41)$$

$$\sin 2\epsilon_1 = \pm \sin 2\epsilon_{10} (1 \pm \Delta S \Delta' \cos 2\epsilon_{10}), \quad (42)$$

where $(\pm)$ and $(-)$ are for $\Psi = \cot \epsilon_{10}$.

Eqs. (41) and (42) show that under these conditions we also can use an elliptically polarized test beam to isolate the real and imaginary parts of the 3NS. In contrast to case of a linearly polarized probe beam the rotation of the polarization ellipse yields $\text{Re } \chi_{1221}$ and the change of ellipticity gives $\text{Im } \chi_{1221}$. It should be noted here that for a linearly polarized test beam ($\epsilon_{10}=0$) with the above mentioned input azimuths in accordance with eqs. (41) and (42) the effect of the probe wave polarization change vanishes. However, introducing a small ellipticity to input linear polarization of the probe beam we can considerably increase the effectiveness of nonlinear interaction. It is demonstrated in ref. 22 for

some dye solutions.

2.3 Circularly polarized pump

In this case the eigenvectors of tensor $\hat{S}$ are $R(\vec{e}_+)$ and $L(\vec{e}_-)$. The corresponding eigenvalues are given as

$$S_1 = 1 + C_1, \quad S_2 = 1 + C_2 \quad (43)$$

$$\text{and} \quad \Delta S = C_2 - C_1. \quad (44)$$

Then for linearly polarized probe beam with initial azimuth Θ_{10} ($\chi_{10} = \exp(-i2\Theta_{10})$) from eqs. (19) and (20) we have

$$\Theta_1 = \Theta_{10} + \frac{1}{2} \Delta S \Delta'', \quad (45)$$

$$\eta_1 = \tanh\left(\frac{1}{2} \Delta S \Delta'\right). \quad (46)$$

Thus, NSE with circularly and linearly polarized pump and probe beams, respectively, permits to investigate the Im and Re parts of the 3NS separately too. As in the previous case (§ 2.2.3) the real part of the cubic susceptibility rotates the plane of polarization of the probe beam, while the imaginary part gives rise to the ellipticity. It should be noted that the resembling results recently have been obtained in ref. 23 on the basis of more formal approach and, hence, as it has been mentioned by authors, with coefficients in the corresponding equations that are not easily obtained for experimental situation. It is also interesting that eqs. (45) and (46) formally do not include any oscillatory functions like $\sin(x)$ and $\cos(x)$ in the linearly polarized pump case.

2.4 Elliptically polarized pump

In this subsection we will distinguish two cases: $C_1 = C_2$ and these parameters are not equal to one another.

2.4.1 $C_1 = C_2 = C$

This means that $\chi_{1122} = \chi_{1212}$. The latter one occurs in many rigid dye solutions²⁴⁾. Moreover, for them $C = 1$ (Kleinman symmetry). In this case the tensor $\hat{S}$ is diagonalized in the basis $(\vec{e}_x, \vec{e}_y)$ as for a linearly polarized pump. However the corresponding eigenvalues become

$$S_1 = 1 + 2C \cos \epsilon_0, \quad S_2 = 1 + 2C \sin^2 \epsilon_0 \quad (47)$$

$$\text{and} \quad \Delta S = -2C \cos 2\epsilon_0. \quad (48)$$

Here ϵ_0 is the ellipticity angle of the pump beam. Thus, we can use all equations of § 2.2 with corresponding replacement of ΔS . It should be noted here that under conditions of the circularly polarized excitation ($|\epsilon| = \pi/4$) the tensor $\hat{S}$ becomes degenerate ($S_1 = S_2$) and any polarization of the probe beam remains unchanged (see eq. (14)).

2.4.2 $C_1 \neq C_2$

In this case the eigenvectors of the tensor $\hat{S}$ have the orthogonal states of elliptical polarization⁹⁾. The corresponding transformation matrix $\hat{F}$ from Cartesian basis to the basis of eigenvectors of the tensor $\hat{S}$ has the form⁹⁾

$$\hat{F} = \cos^{-1} 2\gamma \begin{pmatrix} \cos \gamma & -\sin \gamma \\ -\sin \gamma & \cos \gamma \end{pmatrix} \quad (49)$$

where

$$\sin 2\gamma = i \frac{C_2 - C_1}{C_1 + C_2} \tan 2\epsilon = i q \tan 2\epsilon = i \mathcal{A}. \quad (50)$$

Now the bilinear transformation (21) becomes

$$\chi_{1xy} = \frac{\cos \gamma \chi_{10uv} \exp(\Delta S \Delta) - \sin \gamma}{-\sin \gamma \chi_{10uv} \exp(\Delta S \Delta) + \cos \gamma}, \quad (51)$$

where χ_{10uv} is given as

$$\chi_{10uv} = \frac{\frac{\sin(\gamma + \Theta_{10})}{\cos(\gamma - \Theta_{10})} + i \tan \epsilon_{10} \frac{\cos(\gamma + \Theta_{10})}{\cos(\gamma - \Theta_{10})}}{1 - i \tan \epsilon_{10} \tan(\gamma - \Theta_{10})}. \quad (52)$$

The polarization changes of the probe beam in the field of pumping with an arbitrary elliptic polarization are obtained by direct use of eqs. (51) and (52). However a calculation of this sort in general case is quite laborious. Therefore we will consider only more wide-spread cases when a probe beam is linearly polarized (along $\vec{e}_x$, $\vec{e}_y$ and at 45° to the major axis of an elliptically polarized pump).

2.4.2.1 Linearly polarized probe beam along $\vec{e}_x$ and $\vec{e}_y$

In this case

$$\begin{aligned} \chi_{10uv} &= \tan \gamma & \text{for } \Theta_{10} = 0, \\ \chi_{10uv} &= \cot \gamma & \text{for } \Theta_{10} = \pi/2. \end{aligned}$$

Then in approximation of the first order in Δ and γ it is easily to obtain the corresponding equations for $\Delta \Theta_1$ and γ_1

$$\Delta \Theta_1 \simeq \mp \frac{1}{2} \Delta S \Delta' \mathcal{A}, \quad (53)$$

$$\gamma_1 \simeq \pm \frac{1}{2} \Delta S \Delta' \mathcal{A}, \quad (54)$$

where the upper and lower signs correspond to the input polarization of the probe beam along $\vec{e}_x$ and $\vec{e}_y$, respectively, and

$$\Delta S = -\{(C_1 + C_2)^2 - 4 \sin^2 2\epsilon C_1 C_2\}^{1/2}. \quad (55)$$

Thus, as in the circularly polarized pump case the induced rotation is due to $\text{Re } \chi_{1221}$ and spectral dependence of induced ellipticity is defined by $\text{Im } \chi_{1221}$. It is interesting to note that the handedness of the test beam polarization ellipse

depends on the initial azimuth Θ_{10} .

2.4.2.2 Linearly polarized probe beam at $\Theta_{10} = 45^\circ$

Then $\chi_{10uv} = 1$ and for parameters Δ , Θ_1 and ϵ_1 we can obtain

$$\cot \Delta \Theta_1 = \frac{2 \exp(\Delta S \Delta') \cos(\Delta S \Delta'')}{1 - \exp(2 \Delta S \Delta')}, \quad (56)$$

$$\sin 2 \epsilon_1 = \frac{2 \exp(\Delta S \Delta') \sin(\Delta S \Delta'') - \Delta E}{1 + \exp(2 \Delta S \Delta')}, \quad (57)$$

where we assumed that $|\gamma| \ll 1$. The last condition restricts the value of the pump beam ellipticity. However in dye solutions, as a rule, the ratio q is small²⁴⁾ (e. g., for malachite green in water¹⁾ $q \simeq \text{Re} q = 0.14$) and the choice of γ H can be rather free. Eqs. (56) and (57) show that the polarization ellipse rotation is the same as in the case of linearly polarized pumping and only induced ellipticity depends on ΔE . It should be noted that in approximation that is linear in Δ and γ the polarization behavior of the probe field is described by the eqs. (33) and (34) and, hence, use of the linearly polarized pump is more preferable for purposes of NSE because this polarization is fairly stable²⁵⁾.

2.5 Numerical estimations of the 3NS of some substances in the framework of NSE

At the beginning we consider the case when both probe and pump beams interact with the same electronic transition of the resonance medium. To our knowledge, there are only two papers devoted to the experimental investigations of the test beam polarization under these conditions. We will analyze the data of ref. 26 and 27 for 3-amino-N-methylphthalimide in

glycerol and for cryptocyanine in ethanol, respectively. The orthogonal excitation was used in both experiments. Then we should consider only the transverse component of the tensor $\hat{S}$ that is given as⁹⁾

$$\hat{S} = \hat{I} - \vec{n}_1 \otimes \vec{n}_1 + (C_1 + C_2) |(\vec{n}_1 \times \vec{n}_0) \cdot \vec{e}_0|^2 (\vec{n}_1 \times \vec{n}_0) \otimes (\vec{n}_1 \times \vec{n}_0). \quad (58)$$

Here $\vec{n}_0$ and $\vec{n}_1$ are the unit vectors along the directions of propagation which in our case are defined as $\vec{n}_0 = \vec{e}_y$ and $\vec{n}_1 = \vec{e}_z$. Now, assuming that the Kleinman relations are valid in these dye solutions (i. e., $C_1 = C_2 = 1$) and $\vec{e}_0 = \vec{e}_x$, we get $\Delta S = -2$. Further using the prescribed-field approximation for parameter β we have

$$\beta = \frac{3}{4} \frac{\omega_1}{cn_1} |\vec{E}_0|^2_z. \quad (59)$$

From eqs. (33) - (34) and (59) and data of ref. 26 we can calculate Re and Im parts of the component χ_{1221} of the 3NS. The corresponding values we collected in Table 1. The authors²⁶⁾ have examined the optical anisotropy in solutions of polyatomic molecules due to orientational ordering in the excited state. They did not observe any phase anisotropy which would produce elliptical polarization according to eq. (34). This means that Re χ_{1221} is negligible under these conditions. Contrary to the ref. 26 in ref. 27 only induced birefringence of a standard solution of cryptocyanine has been investigated. The wavelength and power of the probe beam were chosen so that there should be no noticeable amplitude changes in the excited volume of sample. The signal behind the crossed analyzer was due to only induced elliptical polarization of the input linearly polarized sounding wave. Then for light-induced linear birefringence we have (see Appendix)

$$\Delta n = -\frac{3}{cn_1 \epsilon_0} I_0 \operatorname{Re} \chi_{1221}, \quad (60)$$

where I_0 is the pump beam intensity.

Direct substitution into eq. 60 of the following values from ref. 27 $\Delta n = 7 \times 10^{-6}$ and $I_0 = 60 \text{ MW/cm}^2$ yields $\operatorname{Re} \chi_{1221} \simeq -1 \times 10^{-13} \text{ esu}$.

Thus, the 3-amino-N-methylphthalimide dye is considerably more effective for investigating the nonlinear optical effects. Its values of the 3NS are extremely large. They are comparable to the values of the degenerate cubic susceptibility of some semiconductors and benzoporphyrins measured in ref. 28 and 29, respectively, and roughly 4-5 orders of magnitude greater than the corresponding components of nondegenerate $\hat{\chi}^{(3)}$ for bensene (C_6H_6) and carbon disulphide (CS_2)³⁰. The latter medium is conventionally used for fast optical shutters and correlators.

Finally we make some estimations for condensed and gaseous atomic media under conditions of two-photon and double resonance, respectively. In the first case the absorption (and correspondingly the dichroism) is strongly inhibited and the induced gyrotropy (circular birefringence) leads to a simple rotation of the plane of polarization of the test beam. Then using eqs. (45) and (59) for the ethanol R6G dye solution³¹ we calculated $\operatorname{Re} (\chi_{1212} - \chi_{1122}) \simeq 1 \times 10^{-11} \text{ esu}$ and $\sim 2 \times 10^{-9} \text{ esu}$ for sodium vapor³². Here we took into account that

$$\Delta S = (\chi_{1212} - \chi_{1122}) / \chi_{1221}.$$

In the case of Ne gas as a three-level cascade ($J=0 \rightarrow J=1 \rightarrow J=0$) system³³ we were able to estimate the order of the values which are situated in Table 1 (the estimations were made for $\Delta \Theta_1 \simeq 0.6^\circ$ and $\eta_1 \simeq 0.04$). These values are also very large and comparable with the magnitudes of the transient effective 3NS of the stilbene derivative ($10^{-7} - 10^{-6} \text{ esu}$) that has been reported in ref.

34. The large increase in the 3NS of gaseous media in spite of relatively low vapor densities in comparison with condensed substances is achieved due to a resonant enhancement of the LIA dispersion.

3. Conclusions

We suggested a new variant of NPS dealt with an analysis of the weak wave polarization effects in the media with LIA. The basic relations for the polarization parameters of the test beam have been derived in the general case of arbitrary polarized the probe and pump fields. In the framework of the 3NS, is demonstrated a feasibility of separate investigations of the real and imaginary parts of the nondegenerate 3NS. A new method of measuring the ratio of the real and imaginary parts of the 3NS is proposed. This method is based on using the circularly polarized probe beam under the linearly polarized excitation. Then the above mentioned ratio is equal to azimuth of the induced probe wave elliptic polarization. A possibility of measuring the light-induced linear, circular and elliptic birefringence and dichroism using the standard ellipsometric techniques is pointed out. Finally the numerical estimations of the 3NS are made on the basis of derived relations and the literature data. Comparing with experimental methods of measuring the 3NS of other authors we would like to stress some advantages of the NSE method. First, a few known methods (see ref. 18 and references there) use very delicate techniques and therefore they are fairly complicated. Second, others are interferometric methods, and it seems difficult to obtain information on the nondegenerate 3NS with them. At last, many methods permit to measure only the effective value of the 3NS (e. g., in refs. 34 and 35) although, it is more important to get the values of the separate components $\chi^{(3)}$. It

Table 1. Estimated values of the real and imaginary parts of the 3NS for some substances

Substance	!	λ_0	!	λ_1	!	$\text{Im } \chi_{1221}(-\omega_1; \omega_1, \omega_0, -\omega_0)$	!	$\text{Re } \chi_{1221}(-\omega_1; \omega_1, \omega_0, -\omega_0)$
	!	(nm)	!	(nm)	!	(esu)	!	(esu)
3-amino-N-methyl-	!	347	!	490	!	-3×10^{-10}	!	? * *)
phtalimide in	!	347	!	500	!	-3×10^{-10}	!	?
glycerol	!	347	!	510	!	-1×10^{-9}	!	?
cryptocyanine	!	694	!	900	!	?	!	-1×10^{-13}
in ethanol	!		!		!		!	
	!		!		!	$\text{Im}(\chi_{1212} -$	!	$\text{Re}(\chi_{1212} -$
	!		!		!	$-\chi_{1122})$	!	$-\chi_{1122})$
	!		!		!	(esu)		(esu)
R6G in ethanol	!	1064	!	1064	!	?	!	1×10^{-11}
Na vapor	!	615.9	!	589.1	!	?	!	2×10^{-9}
neon	!	609.4	!	633.0	!	$10^{-7} - 10^{-8}$	!	$10^{-7} - 10^{-8}$

* *) " ? " denotes the value which, at least, considerably less than evaluated one to a given substance. The corresponding kind of anisotropy (birefringence or dichroism) has not been detected experimentally.

should be mentioned also that the majority of known methods does not permit independent measuring the Re and Im parts of the 3NS (see, for example, recent paper³⁶⁾). Our analysis shows that the NSE method of measuring the 3NS is free from these drawbacks.

Appendix

This Appendix aims at definition of magnitude of the light-induced birefringence and dichroism in isotropic media. As Azzam et al. we will consider an optical device in the form of a thick slab of an anisotropic medium (in our case-a medium with LIA). Then the relation between Jones matrix $\hat{T}$ of such a device and the differential propagation Jones matrix $\hat{N}$ (8) that describes its internal properties is given by a differential equation

$$\hat{N}(z) = \frac{d\hat{T}(z)}{dz} \hat{T}^{-1}(z) \quad (\text{A1})$$

For our case the solution of eq. (A1) can be represented in the form of matrix exponential

$$\begin{aligned} \hat{T}(z) &= \exp \left\{ \int_0^z \hat{N}(\xi) d\xi \right\} \\ &= \exp \left(-\frac{1}{2} \sigma_{1z} \right) \exp \{ \hat{S}A(z) \} \\ &= \exp [\hat{M}(z)], \end{aligned} \quad (\text{A2})$$

where $A(z)$ is defined by eqs. (15) and (26).

Now, if the eigenpolarizations of the optical system given by matrix $\hat{T}$, are known, we can perform the ellipsometric measurements of the ratio of corresponding eigenvalues. It should be noted that matrices $\hat{M}$ and $\hat{T}$ have the same eigenvectors (as $\hat{S}$) and their eigenvalues are related by the expression³⁷⁾

$$T_i(z) = \exp \{ M_i(z) \}, \quad (\text{A3})$$

where T_i and F_i are the eigenvalues of matrices

$\hat{T}(z)$ and $\hat{M}(z)$ respectively. Thus, the ratio of eigenvalues is

$$\rho = \frac{T_u}{T_v} = \exp(-\Delta S \Delta) = t \exp(i\sigma), \quad (A4)$$

where

$$t = \exp\{-2\pi z \Delta \alpha / \lambda_1\}, \quad (A5)$$

$$\delta = -\frac{2\pi}{\lambda_1} z \Delta n. \quad (A6)$$

Here $\Delta \alpha$ and Δn represent the linear, circular or elliptic dichroism and birefringence of the medium with LIA under excitation by a linearly, circularly or elliptically polarized light, respectively. However we note that the polarization of the eigenvectors $\vec{e}_u$ and $\vec{e}_v$ depends not only the polarization of the pump field but on the direction $\vec{n}_0$ and $\vec{n}_1$ and the properties of the medium too⁹⁾. For example, in the majority of rigid dye solutions the elliptically polarized collinear pump induces linear birefringence and dichroism (see § 2.3.1.). Further from eqs. (A4)–(A6) we have for $\Delta \alpha$ and Δn

$$\Delta \alpha = -\frac{\lambda_1 \Delta S}{2\pi z} \beta \operatorname{Im} \chi_{1221}, \quad (A7)$$

$$\Delta n = \frac{\lambda_1 \Delta S}{2\pi z} \beta \operatorname{Re} \chi_{1221}, \quad (A8)$$

where ΔS is defined for a linear, circular and elliptic anisotropy by eqs. (24), (44) and (57), respectively.

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